



In re Patent Application of:

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For: CATALYST FOR USE IN PRODUCING LOWER FATTY ACID ESTER,  
PROCESS FOR PRODUCING THE CATALYST, AND PROCESS FOR  
PRODUCING LOWER ALIPHATIC CARBOXYLIC ACID ESTER USING THE  
CATALYST

TRANSLATOR'S DECLARATION

Honorable Commissioner of Patents & Trademarks  
Washington, D.C. 20231

Sir:

I, Tsuguo Yoshida, residing at c/o A. AOKI, ISHIDA &  
ASSOCIATES, Toranomom 37 Mori Bldg., 3-5-1, Toranomom Minato-  
ku, Tokyo 105-8423, Japan declare the following:

- (1) That I know well both the Japanese and English  
languages;
- (2) That I translated Japanese Patent Publication  
No. 57-130954, published August 13, 1982, from the Japanese  
language to the English language;
- (3) That the attached English translation is a true and  
correct translation of the aforesaid Japanese Patent  
Publication No. 57-130954 to the best of my knowledge and  
belief; and
- (4) That all statements made of my own knowledge are true  
and that all statements made on information and belief are  
believed to be true, and further that these statements are made  
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18 U.S.C. 1001, and that such false statements may jeopardize  
the validity of the application or any patent issuing thereon.

November 10, 2004  
Date

Tsuguo Yoshida  
Translator Tsuguo Yoshida

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(54) ESTERIFICATION METHOD

## Specification

1. TITLE OF THE INVENTION Esterification Method
2. CLAIMS

An esterification method characterized by using a carrier-supported catalyst comprised of a catalyst constituted by a heteropolyacid or its salt supported on active carbon when reacting an acid and an alcohol to produce an ester.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a novel esterification method. More particularly, it is an esterification method using a carrier-supported catalyst comprised of a catalyst constituted by a heteropolyacid or its salt supported on active carbon when reacting an acid and an alcohol to produce an ester.

In the past, use of a heteropolyacid or its salt as a catalyst for various reactions has been known. For example, when performing a reaction in a uniform liquid phase system in which a heteropolyacid is dissolved, after the reaction, the heteropolyacid has had to be separated and recovered from the reacted substance without allowing the heteropolyacid catalyst to be changed by removing the reaction product, unreacted substances, solvent, etc. by distillation or another procedure to recover the heteropolyacid or using ether etc. to change the heteropolyacid to an insoluble complex and separating it. That is, not only is the method of separating and recovering the heteropolyacid used as a catalyst from the reacted matter complicated in procedure, but also there have been difficult problems such as the reaction product causing secondary reactions in the middle of the separation and recovery. Further, use of a heteropolyacid supported on a carrier has been attempted for several reactions, but elution of the heteropolyacid from the carrier has not been able to be completely prevented and commercialization has not been achieved. Therefore, when performing a liquid phase reaction or gas phase reaction in the presence of a medium dissolving a heteropolyacid or its salt such as water, alcohol, a ketone, an ether, or a carboxylic acid, in what form to handle the catalyst comprised of the heteropolyacid or its salt is an important technical issue.

On the other hand, the esterification method of reacting an acid and an alcohol to produce an ester has been industrially practiced since long in the past. In this esterification method, in general, as the catalyst, sulfuric acid, hydrochloric acid, toluenesulfonic acid,

borotrifluoride, an acidic ion exchange resin, or other acid catalyst has been used. However, these catalysts have the defects of the difficulty in separation and recovery of the catalyst, the lack of a property of heat resistance, etc., so cannot necessarily be said to be satisfactory.

The inventors engaged in repeated research on various reactions regarding the catalytic activity of heteropolyacids and their salts. As a result, they learned that even in an esterification reaction using a solvent dissolving a heteropolyacid or its salt such as an acid, alcohol, or water, when using a specific carrier-supported catalyst, it is possible to execute the reaction continuously without seeing any elution of the heteropolyacid or its salt. After this, they continued with further research and as a result confirmed that if using a carrier-supported catalyst comprised of a heteropolyacid or its salt supported on active carbon as the catalyst of the esterification reaction, not only is there no elution of the heteropolyacid or its salt to the reaction system, but also byproducts such as ether due to the dehydration of the alcohol is remarkably suppressed and the ester is produced with a good yield and thereby completed the present invention.

That is, the present invention is an esterification method using a carrier-supported catalyst comprised of a catalyst constituted by a heteropolyacid or its salt supported on active carbon when reacting an acid and an alcohol to produce an ester.

The biggest feature of the present invention is the use of a carrier-supported catalyst comprised of a heteropolyacid or its salt supported on active carbon. The

method of getting the heteropolyacid or its salt to be supported on active carbon is not particularly limited. A known method may be used. The generally advantageously used method is to dissolve in water, alcohol, an ether, a carboxylic acid, or other organic solvent dissolving a heteropolyacid or its salt a predetermined amount of the heteropolyacid or its salt, adding into the solvent a predetermined amount of active carbon, then causing the heteropolyacid or its salt to be adsorbed at the active carbon while sufficiently stirring at ordinary temperature or under the boiling point of the solvent for the necessary time, for example, 30 to 60 minutes. After this, the active carbon is filtered out from the organic solvent, then the result is washed or extracted by a solvent at ordinary temperature or below the boiling point until elution of the heteropolyacid or its salt can no longer be observed and if necessary drying is performed, whereby the carrier-supported catalyst of the present invention is obtained. The supported amount of the heteropolyacid or its salt conditional on being supported on active carbon and not being eluted during the covered reactions differs depending on the type of the heteropolyacid, the properties of the active carbon, etc. and cannot be generally limited, but in general is preferably made not more than 20 (wt)%. If the supported amount is great, not only do the esters and other byproducts increase, but also washing or extraction at the time of preparing the catalyst takes a long time. Sometimes the heteropolyacid will be reduced until a certain supported amount or the heteropolyacid will elute in the middle of the reaction, so it is preferable to test out the maximum amount of the supported amount in advance. The most

generally used supported amount of the heteropolyacid or salt is in the range of 5 to 20 (wt)%, preferably 10 to 15 (wt)%.

The active carbon used in the present invention is not particularly limited. A known one or a commercially available one may be used as it is or if necessary treatment by nitric acid or activation may be performed for use. Further, the heteropolyacid or its salt used in the present invention is not particularly limited. Any known one may be used. If illustrating typical ones preferably used, there are 12-molybdophosphoric acid, 12-tungstophosphoric acid, 12-molybdosilicic acid, 12-tungstosilicic acid, 12-tungstoboric acid, 12-tungstogermanic acid, 11-molybdophosphoric acid, and their salts, for example, salts of metals of Group I, Group II, Group III, and Group IV of the Periodic Table.

With the carrier-supported catalyst comprised of the above heteropolyacid or its salt supported on active carbon, even in a reaction system with the presence of a medium able to dissolve the heteropolyacid or its salt, there is no elution of the catalyst ingredient into the medium and a good catalytic activity can be exhibited for use for a long period. How these effects function and are exhibited with the active carbon or the heteropolyacid or its salt alone or in combination is still not clear at the present, but it is guessed that the heteropolyacid or its salt supported on the specific carrier of active carbon is extremely strongly adsorbed or is bonded by some sort of chemical bond since it is not eluted even with a solubilizing medium. This can be said to be an extremely special phenomenon.

The reactions covered involving a carrier-supported catalyst of the present invention are not particularly limited so long as they are esterification reactions. The invention can be applied to known esterification reactions, for example, reactions stripping water from organic acids or inorganic acids and alcohol to produce esters. The esterification reactions to which this is most generally applied are reactions between formic acid, acetic acid, propionic acid, acrylic acid, phthalic acid, or other organic carboxylic acids and methyl alcohol, ethyl alcohol, propyl alcohol, or other aliphatic alcohols. When using said carrier-supported catalyst for these esterification reactions, the catalytic activity is exhibited extremely well, so a good function as a solid acid catalyst is exhibited not only for a liquid phase reaction, but also a gas phase reaction. Therefore, in general, the catalyst is used in a wide temperature range from low temperature to high temperature, but most preferably the reaction system is heated to the boiling point or close to the boiling point or a gas phase reaction is performed.

As explained above, in the reactions covered by the present invention, the catalyst ingredient is never eluted from the carrier-supported catalyst, so there are the advantages that use as a solid acid catalyst is possible, separation of the reaction product, unreacted substances, etc. and the catalyst is extremely easy, and the reactions can be performed by industrially simple procedures.

The present invention will be explained more specifically below by an explanation giving examples and comparative examples, but the present invention is not limited to these examples.

### Example 1

Active carbon (F-300) made by Calgon Co. was pulverized to 35 to 60 mesh, sufficiently rinsed, then dried at 100°C for 6 hours. 12-tungstosilicic acid was dissolved in 100 cc of water, 5.0 g of the above dried active carbon was added to this, then the 12-tungstosilicic acid was made to be adsorbed at the active carbon while refluxing for 1 hour. The result was cooled, then the active carbon was filtered out, rinsed at ordinary temperature by 200 ml of water, then extracted under the boiling point of water using a Soxhlet extractor until 12-tungstosilicic acid could no longer be detected in the extract. As a result, the extraction time until 12-tungstosilicic acid could no longer be detected was 30 hours, and the amount of 12-tungstosilicic acid supported on the active carbon was 18 (wt)% before the extraction treatment and 10.8 (wt)% after the extraction treatment.

1.0 ml of active carbon supporting 10.8 (wt)% of 12-tungstosilicic acid obtained in this way was packed into the center part of a Pyrex glass reaction tube of an inside diameter of 1.5 cm and a length of 30 cm, then a mixture of ethanol and acetic acid (ethanol:acetic acid molar ratio of 2.5:1) was passed through it at 150°C by an LHSV = 0.9 h<sup>-1</sup>. As a result, ethyl acetate was obtained with a conversion rate of acetic acid of 96%, a selectivity of acetic acid of 100%, and a selectivity of ethanol of 99.9%. After this, the reaction was performed continuously for 7 hours. As a result, the conversion rate and the selectivities did not change at all. Further, the catalyst ingredient, that is, 12-tungstosilicic acid, could not be detected at all in the reaction product. For comparison, active carbon not



carrying any 12-tungstosilicic acid was used to conduct the reaction by a similar procedure. As a result, the conversion rate of acetic acid was only 20%.

Further, for comparison, silica gel (Waco, Q-22) on which 12-tungstosilicic acid in an amount of 10.8 (wt)% was supported was used as a catalyst and a reaction was conducted under a similar reaction procedure and conditions. As a result, ethyl acetate was observed with a conversion rate of acetic acid of 93% and a selectivity of acetic acid of 100%, but with a selectivity of ethanol to ethyl acetate of 71%, a large amount of diethyl ether was secondarily produced.

#### Example 2

Instead of the 12-tungstosilicic acid and reaction starting materials used in Example 1, the ones shown in Table 1 were selected. Otherwise, the same procedure was followed as in Example 1 to prepare catalysts. An esterification reaction was performed under the same reaction conditions as in Example 1 with a molar ratio of alcohol:acid of 2.5:1. The results were as shown in Table 1. In each case, no ether byproducts could be observed.

	Heteropolyacid		Type of starting material		Reaction product		
	Type	Supported amount wt%	Acid	Alcohol	Type	Conversion rate of acid %	Selectivity of acid %
1	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	9.3	Acetic acid	Ethanol	Ethyl acrylate	83	100
2	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	10.0	"	"	"	75	100
3	H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	10.0	"	"	"	73	100
4	NaH <sub>3</sub> SiW <sub>12</sub> O <sub>40</sub>	10.0	"	"	"	95	100
5*	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	10.8	Acetic acid	n-butanol	n-butyl acetate	96	100
6	"	10.8	Acrylic acid	Ethanol	Ethyl acrylate	65	95
7	"	10.8	Benzoic acid	Methanol	Methyl benzoate	100	100

\* 0.2 (wt)% of hydroquinone added to reaction starting material.

### Example 3

Instead of the water in Example 1, methanol was used to prepare the catalyst. As a result, the extraction time until 12-tungstosilicic acid was no longer detected was 5 hours, and the amount of 12-tungstosilicic acid supported at the active carbon was 9.3 (wt)% before the extraction treatment and 8.4 (wt)% after the extraction treatment.

1.0 ml of active carbon carrying 8.4 (wt)% of 12-tungstosilicic acid obtained in this way, 10 ml of methanol, and 3.7 g of phthalic anhydride were mixed and stirred for reaction under the boiling point of methanol for 2 hours. As a result, 55% of the charged phthalic anhydride was converted to dimethyl phthalate. No elution of 12-tungstosilicic acid from the catalyst could be observed at all.